



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US98/03358 <b>(22) International Filing Date:</b> 20 February 1998 (20.02.98)  <b>(30) Priority Data:</b> 08/812,092                      4 March 1997 (04.03.97)                      US  <b>(71) Applicant:</b> HERCULES INCORPORATED [US/US]; Intellectual Property Section, 8th floor, 1313 North Market Street, Wilmington, DE 19894-0001 (US).  <b>(72) Inventor:</b> GAST, John, C.; 10 Kings Grant Road, Hockessin, DE 19707 (US).  <b>(74) Agent:</b> SLOAN, Martin, F.; Hercules Incorporated, Intellectual Property Section, 8th floor, 1313 North Market Street, Wilmington, DE 19894-0001 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> HYDROPHOBICALLY MODIFIED RESIN COMPOSITIONS AND USES THEREOF  <b>(57) Abstract</b>  Resin compositions that are the reaction product of epihalohydrin and hydrophobically modified aminoamide obtained by the reaction of: (a) aminoamide containing at least one primary amine group and at least one secondary and/or tertiary amine groups, the aminoamide being obtained by reaction of polyamine containing at least two primary amine groups and at least one secondary and/or tertiary amine group, with dicarboxylic acid or derivatives thereof, wherein the molar ratio of polyamine to dicarboxylic acid or derivative thereof, is greater than about 1.4:1, and, (b) hydrophobizing agent having from about 12 to about 40 carbon atoms, wherein the amount of hydrophobizing agent employed is sufficient to react with at least a portion of the primary amine groups, but insufficient to react with more than about 60 % of the secondary and/or tertiary amine groups of the aminoamide. Also disclosed are uses of the compositions in the treatment of paper, particularly the sizing of paper.		

## **HYDROPHOBICALLY MODIFIED RESIN COMPOSITIONS AND USES THEREOF**

### **Field of the Invention**

5 This invention relates to hydrophobically modified epihalohydrin-  
aminoamide resins and their uses.

### **Background of the Invention**

A variety of materials has been used in the paper making art for surface  
sizing paper. These include alkyl ketene dimers, styrene-maleic anhydride  
(SMA) polymers, and epichlorohydrin-modified bis-stearamides. Each of these  
10 has serious deficiencies in use. For example, both the alkyl ketene dimers and  
the bis-stearamides significantly lower the coefficient of friction of paper when  
applied to the surface. This adversely affects the performance of the paper in  
high speed converting operations. Moreover, the bis-stearamides have a  
negative effect on the tensile properties of the paper. SMA solution polymers  
15 are foamy, can be supplied only at low solids, and give only limited sizing in  
some grades. Moreover, SMA polymers are ineffective when applied over  
paper that does not have internal sizing.

The materials of the present invention do not cause deterioration of the  
tensile properties of the paper to which they are applied, nor do they cause a  
20 significant reduction in coefficient of friction. They also do not foam  
excessively and are highly effective sizing agents, even when applied over  
paper that does not have internal sizing.

U.S. Patent No. 3,922,243 to Aldrich et al. discloses water-insoluble,  
water-dispersible thermosetting cationic resins derived by reaction of a water-  
soluble aminopolyamide, a hydrophobizing compound and an epihalohydrin.  
25 The aminopolyamide contains secondary amine groups and is prepared using a  
mole ratio of polyalkylene polyamine to dicarboxylic acid from about 0.9 to

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about 1.2. The amount of hydrophobizing agent is insufficient to react with more than about 50% of the secondary amine groups of the aminopolyamide.

U.S. Patents 3,923,745, 3,968,317 and 3,992,345 to Dumas disclose water-insoluble, water-dispersible thermosetting cationic resins derived by  
5 reaction of a diallylamine polymer, a hydrophobizing compound and epihalohydrin.

### Summary of the Invention

A resin composition comprises the reaction product of epihalohydrin and hydrophobically modified aminoamide obtained by the reaction of:

10 (a) aminoamide containing at least one primary amine group and at least one non-primary amine group selected from the group consisting of secondary and tertiary amine groups, the aminoamide being obtained by reaction of an amine composition comprising polyamine containing at least two primary  
15 amine groups and at least one amine group selected from the group consisting of secondary and tertiary amine groups, with dicarboxylic acid or derivatives thereof, wherein the molar ratio of polyamine to dicarboxylic acid or derivative thereof, is greater than about 1.4:1, and,

(b) hydrophobizing agent having from about 12 to about 40 carbon atoms, wherein the amount of hydrophobizing agent employed is sufficient to  
20 react with at least a portion of the primary amine groups, but insufficient to react with more than about 60% of the non-primary amine groups.

A method for making the resin composition comprises: a) reacting an amine composition comprising polyamine containing at least two primary amine groups and at least one amine group selected from the group consisting  
25 of secondary and tertiary amine groups with dicarboxylic acid, or derivatives thereof, wherein the molar ratio of polyamine to dicarboxylic acid or derivative thereof is greater than about 1.4:1, to form aminoamide containing at least one primary amine group and at least one non-primary amine group selected from the group consisting of secondary and tertiary amine groups;

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b) reacting the aminoamide with hydrophobizing agent having from about 12 to about 40 carbon atoms to form hydrophobically modified aminoamide,

5 wherein the amount of hydrophobizing agent employed is sufficient to react with at least a portion of the primary amine groups, but insufficient to react with more than about 60% of the non-primary amine groups of the aminoamide; and

c) reacting the hydrophobically modified aminoamide with epihalohydrin.

10 A method for sizing paper comprises adding to the surface of paper sheet an aqueous suspension of the resin composition. Another method for sizing paper comprises the steps of (a) providing an aqueous pulp suspension; (b) adding to the aqueous pulp suspension an aqueous suspension of the resin composition;

15 (c) forming the pulp into a sheet; and (d) drying the sheet to obtain sized paper.

### Detailed Description of the Invention

The aminoamides used in preparing the resin compositions are derived by reaction of dicarboxylic acid or derivatives thereof, and polyamine containing at least two primary amine groups and one or more secondary or

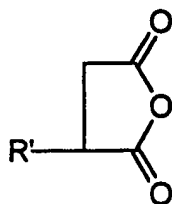
20 tertiary amine groups. Dicarboxylic acid derivatives suitable for preparing the aminoamides include esters, anhydrides and acid halides.

Dicarboxylic acids for use in preparing the aminoamides include aliphatic, alicyclic or aromatic dicarboxylic acids, or their derivatives, containing from 2 to about 44 carbon atoms. Preferably the dicarboxylic acids

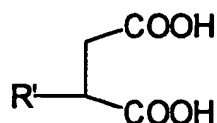
25 are selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, fumaric acid, maleic acid, phthalic acid, terephthalic acid, diglycolic acid, C<sub>36</sub>-C<sub>44</sub> dimer acids, alkenyl succinic acids and alkyl succinic acids. More preferably, the dicarboxylic acids are adipic acid and alkenyl succinic acids.

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$C_{36}$ - $C_{44}$  dimer acids are derived by dimerizing or polymerizing naturally occurring unsaturated fatty acids and are available as EMPOL® dimer acid, from Henkel-Emery, Cincinnati, Ohio. Alkenyl succinic acids, or anhydrides, are available by reaction of maleic anhydride with straight chain or branched olefins, and have the following general structures I and II



(I)



(II)

wherein R' is a straight chain or branched, unsaturated alkyl radical having from about 8 to about 22 carbon atoms, preferably from about 16 to about 22 carbon atoms. Alkyl succinic acids or anhydrides may be prepared by hydrogenation of the corresponding alkenyl succinic acid or anhydride. Specific examples of anhydrides of formula I are isooctadecenyl succinic anhydride, n-octadecenyl succinic anhydride, n-hexadecenyl succinic anhydride, n-dodecyl succinic anhydride, i-dodecenyl succinic anhydride, n-decenyl succinic anhydride, n-octenyl succinic anhydride, and isobutylene oligomers succinic anhydride. The corresponding acids of formula II are derivable from the anhydrides by hydrolysis.

Preferably, at least 50 mole % of the amine composition used for reaction with the dicarboxylic acid will be polyamine containing at least two primary amine groups and one or more secondary or tertiary amine groups. Preferred polyamines are N-alkyl bis(3-aminopropylamine), wherein the N-alkyl group is an alkyl group containing from 1 to about 12 carbon atoms, and polyalkylene polyamines containing two primary amine groups and at least one

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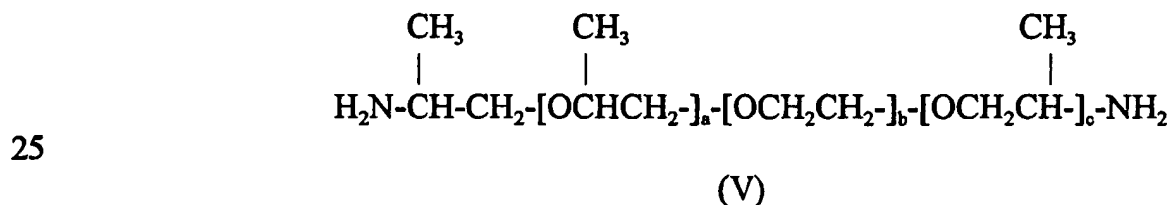
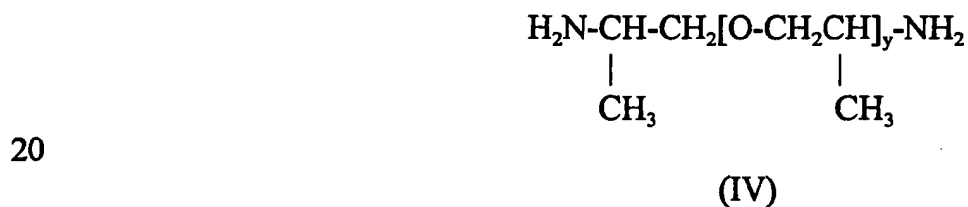
secondary amine group where the nitrogen atoms are linked together by groups of the formula  $-C_nH_{2n}-$ , where n is from 2 to 6.

Preferred polyalkylene polyamines include polyethylenepolyamines, polypropylenepolyamines and polybutylenepolyamines.

5 Polyethylenepolyamines are more preferred. The most preferred polyethylenepolyamines for use in this invention are diethylenetriamine, triethylenetetramine or tetraethylenepentamine. The most preferred is diethylenetriamine.

10 The preferred N-alkyl bis(3-aminopropylamine) is N-methyl bis(3-aminopropylamine).

In addition to the polyamine containing at least two primary amine groups and one or more secondary or tertiary amine groups, the amine composition used for reaction with the dicarboxylic acid may contain other diamines, preferably those having the formulas III, IV and V.



wherein x is an integer from 2 to about 10, y is an integer from 2 to about 100, b is an integer from 2 to about 100, and a and c, which can be the same or different, are integers from 0 to about 5.

Exemplary diamines of formula III are ethylene diamine, propylene diamine, and hexamethylene diamine. Materials corresponding to formulas IV are available as Jeffamine®D-230, D-400, D-2000 and D-4000 from Huntsman Corporation, Houston, Texas. Materials corresponding to formula V are  
5 available as Jeffamine®ED-600, ED-900 and ED-2001 from Huntsman Corporation.

In preparing the aminoamides the amine composition is used in substantial molar excess over dicarboxylic acid. The aminoamides that result contain substantial quantities of primary amine groups, and are oligomeric, i.e.,  
10 contain from about 1 to about 6 repeating units. In order to achieve these properties, the molar ratio of polyamine to dicarboxylic acid is greater than about 1.4 to 1. Preferably, the molar ratios is from about 1.5 to 1 to about 3 to 1, more preferably from about 1.55 to 1 to about 2.5 to 1, and most preferably from about 1.6 to 1 to about 2 to 1.

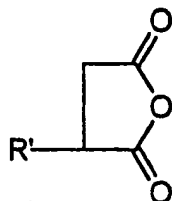
15 Temperatures employed for carrying out the reaction between dicarboxylic acid and amine can vary from about 110°C to about 250°C or higher, at atmospheric pressure. Temperatures between about 160°C and 210°C are preferred. Where reduced pressures are employed, lower temperatures can be utilized, as is well known in the art. Reaction time will usually vary from  
20 about 1/2 to about 2 hours, although shorter or longer reaction times can be utilized depending on reaction conditions. Reaction times vary inversely with temperature.

In preparing the novel resin compositions of this invention, the aminoamide is reacted with at least one compound, referred to hereinafter as a  
25 "hydrophobizing agent", to form a hydrophobically modified, substantially water-insoluble aminoamide. Hydrophobizing agents are compounds having from about 12 to about 40 carbon atoms that will react with the primary and secondary amine groups of the aminoamide to form substantially water-insoluble compounds. Suitable hydrophobizing agents include, e.g., acids,  
30 anhydrides, acid halides, esters and isocyanates.

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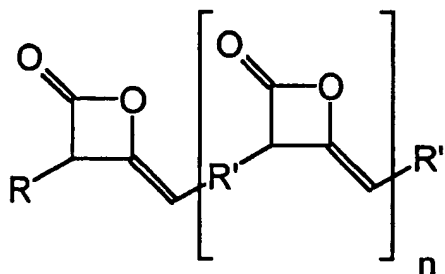
The amount of hydrophobizing agent will be that amount sufficient to react with at least a portion of the primary amine groups, but insufficient to react with more than about 60% of the non-primary amine groups of the aminoamide. Preferably the amount of hydrophobizing agent will be sufficient to react with at least about 20% of the primary amine groups, but insufficient to react with more about 30% of the non-primary amine groups. More preferably the amount of hydrophobizing agent will be sufficient to react with at least 20% of the primary amine groups, but insufficient to react with more than about 10% of the non-primary amine groups.

Examples of preferred hydrophobizing agents are: a) monocarboxylic acids or derivatives thereof, of the formula  $\text{RCOOH}$ , where the R group is alkyl, alkenyl, aryl, cycloalkyl or cycloalkenyl; b) substituted succinic anhydrides of formula I



(I)

where R' is alkyl, alkenyl, cycloalkenyl, aralkyl or aralkenyl groups containing from about 8 to about 22 carbon atoms; and c) ketene dimer or multimer of structure VI



(VI)

where n is an integer of 0 to about 20, R and R'', which may be the same or different, are saturated or unsaturated straight chain or branched alkyl groups



having 8 to 24 carbon atoms, and R' is a saturated or unsaturated straight chain or branched alkyl group having from about 5 to about 40 carbon atoms.

Suitable derivatives of the carboxylic acids RCOOH include esters, anhydrides, acyl halides and isocyanates. With respect to the group of ketene dimers and multimers of formula VI, ketene dimers are preferred. The most preferred hydrophobizing agents are substituted succinic anhydrides of formula I.

Specific examples of the monocarboxylic acids or derivatives thereof, of the formula RCOOH that can be used are rosin acid, myristic acid, palmitic acid, oleic acid and stearic acid.

Specific examples of the anhydrides of formula I are isooctadecenyl succinic anhydride, n-octadecenyl succinic anhydride, n-hexadecenyl succinic anhydride, n-dodecyl succinic anhydride, i-dodecenyl succinic anhydride, n-decenyl succinic anhydride and n-octenyl succinic anhydride.

Ketene dimers for use in the process of this invention have the structure of formula VI where  $n=0$  and the R and R" groups, which can be the same or different, are hydrocarbon radicals. Preferably the R and R" groups are alkyl or alkenyl groups having at least 6 carbon atoms, cycloalkyl groups having at least 6 carbon atoms, aryl having at least 6 carbon atoms, aralkyl having at least 8 carbon atoms, alkaryl having at least 10 carbon atoms, and mixtures thereof.

More preferably ketene dimer is selected from the group consisting of (a) octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, docosyl, tetracosyl, phenyl, benzyl,  $\beta$ -naphthyl, and cyclohexyl ketene dimers, and (b) ketene dimers prepared from organic acids selected from the group consisting of montanic acid, naphthenic acid, 9,10-decylenic acid, 9,10-dodecylenic acid, palmitoleic acid, oleic acid, ricinoleic acid, linoleic acid, eleostearic acid, naturally occurring mixtures of fatty acids found in coconut oil, babassu oil, palm kernel oil, palm oil, olive oil, peanut oil, rape oil, beef tallow, lard, whale blubber, and mixture of any of the above named fatty acids with each other. Most preferably ketene dimer is selected from the group consisting of octyl,

decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, docosyl, tetracosyl, phenyl, benzyl,  $\beta$ -naphthyl, and cyclohexyl ketene dimers.

Suitable ketene dimers are disclosed in U.S. Patent No. 4,279,794, in United Kingdom Patent Nos. 903,416; 1,373,788 and 1,533,434, and in  
5 European Patent Application Publication No. 0666368 A3.

Ketene dimers are commercially available, as Aquapel® and Precis® sizing agents from Hercules Incorporated, Wilmington, Delaware. Preferred are Aquapel®364 and Precis 787® sizing agents.

Ketene multimers for use in the process of this invention have the  
10 formula VI where n is an integer of at least 1, R and R", which may be the same or different, are saturated or unsaturated straight chain or branched alkyl groups having 8 to 24 carbon atoms, preferably 14 or 16 carbon atoms; and R' is a saturated or unsaturated straight chain or branched alkyl group having from about 5 to about 40 carbon atoms, preferably 5 to about 20 carbon atoms.

15 Ketene multimers are described in: European Patent Application Publication No. 0629741A1, European Patent Application Publication No. 0666368A3 and U.S. Patent No. 5,685,815

The reaction of aminoamide and hydrophobizing agent can be carried out neat or in solvent. It is carried out under relatively mild conditions such  
20 that essentially the only reaction taking place is the reaction of the hydrophobizing agent with the primary and secondary (if present) amine, whereby the amines are converted into amides, ureas,  $\beta$ -ketoamides, imidazolines, or  $\beta$ -amidoacids, depending on the specific hydrophobizing agent and reaction conditions utilized. Thus the aminoamide and hydrophobizing  
25 agent are reacted under atmospheric or higher pressure at a reaction temperature of from about 0°C to about 250°C to produce a reaction product that is essentially water-insoluble. When the hydrophobizing agent is a substituted succinic anhydride of formula I, it is particularly convenient to carry out the reaction in the absence of solvent, and it has been found that the  
30 relatively mild temperature conditions of 100°-150°C are suitable. Reaction of

substituted succinic anhydrides with primary amine may lead to the formation of cyclic imide under sufficiently high temperatures.

The reaction of epihalohydrin, preferably epichlorohydrin, with the water-insoluble reaction product of aminoamide and hydrophobizing agent yields a cationic, hydrophobically modified resin. The reaction with epihalohydrin occurs at the amine groups of the hydrophobically modified aminoamide. It is believed that tertiary amines react with epihalohydrin by initial opening, then reclosure of the epoxide ring with expulsion of the halide ion, to form a glycidyl (2,3-epoxypropyl) ammonium salt; secondary amines react with epihalohydrin to form tertiary aminohalohydrins, which cyclize to form reactive 3-hydroxy-azetidinium salts; and primary amine groups react to form a halohydroxypropyl-substituted secondary amine, which can then react with a second mole of epihalohydrin as described above for secondary amines.

The reaction with epihalohydrin may be carried out in aqueous medium or in solvent. Suitable solvents include: alcohols, e.g., methanol, ethanol, propanol, isopropanol and butanol; benzene; toluene, and the like. Mixtures of two or more solvents can be used if desired. It is to be understood that the solvent employed is non-reactive with the reactants or the reaction product under the reaction conditions.

The reaction with epihalohydrin is carried out at a temperature of from about 0°C to about 100°C, preferably from about 20°C to about 40°C, for a period of time of from about 1/2 hour to about 3 hours (time varies inversely with temperature). The amount of epihalohydrin used will be that amount sufficient to react with at least 40%, preferably at least 70%, and most preferably at least 90% of the amine groups present in the hydrophobically modified aminoamide. The epihalohydrin-reacted composition may be crosslinked by further heating at a temperature of from about 40°C to about 90°C. The solids level of the hydrophobized aminoamide is preferably from about 5% to about 50%.

If the reaction with epihalohydrin is carried out in aqueous medium, the hydrophobized aminoamide may be provided to the reaction as an aqueous dispersion. When the reaction of hydrophobizing agent with aminoamide is carried out molten, such dispersions are readily prepared by adding water to the molten reaction product under agitation. Further dispersion may be accomplished by homogenization.

If reaction with epihalohydrin is to be carried out in solvent, the neat hydrophobized aminoamide can be dissolved in the appropriate solvent prior to the reaction with epihalohydrin. Alternatively, if the hydrophobized aminoamide is prepared in solvent, the product solution may be used for the epihalohydrin reaction directly. Water may be added to the reaction mixture before, during, or after addition of the epihalohydrin.

When water is employed as the reaction medium for carrying out the epihalohydrin reaction, the reaction product (which is a thermosettable cationic resin) in its aqueous reaction medium can be homogenized if necessary to reduce the particle size of the solids. Subsequently, the pH of the dispersion may be adjusted to pH of from about 2.5 to about 8 to provide for optimum stability of the dispersion. In this way stable dispersions having a solids content of from about 5% to about 50% can be prepared.

When the reaction with epihalohydrin is carried out in a solvent other than water, aqueous dispersions of the product can be prepared by the following procedure. The solution of the reaction product is dispersed in water with vigorous agitation such as, for example, by homogenization at pressures of from about 1,000 to 5,000 p.s.i., to provide an aqueous emulsion that is essentially stable. Subsequently, the organic solvent is removed by distillation, either under atmospheric pressure or under vacuum, to provide a stable aqueous dispersion of the reaction product.

The resin compositions of this invention, generally as aqueous dispersions, may be used in the manufacture of paper and other fibrous substrates. Preferably, they are used in the manufacture of surface treated

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paper, particularly surface sized paper by application to the surface of the paper after sheet formation, generally at a size press. They may also be incorporated into a pulp slurry at the wet end of a paper machine to provide sizing or other properties such as, for example, improved pitch dispersion, deposit control, sheet bulk, sheet softness, and size promotion. The amount of resin employed for the sizing of paper will usually be from about 0.05% to about 2% based on the weight of the dry pulp fibers.

After incorporation of the resin compositions of this invention into the paper, either by incorporation into the pulp slurry or by addition to the surface, the resins are cured to a thermoset state by application of heat. Generally the heating will take place during drying of the paper sheet at temperatures of from about 85°C to about 125°C for periods of from about 5 seconds to about 60 seconds. In actual practice, the conventional drum drying of the treated paper sheet will provide for sufficient curing of the resin.

This invention is illustrated by the following examples, which are exemplary only and not intended to be limiting. All percentages, parts, etc., are by weight, based on the weight of the dry pulp, unless otherwise indicated.

### Example 1

This example illustrates the preparation of an aminoamide from adipic acid and diethylenetriamine and its reaction with the hydrophobizing agent hexadecenylsuccinic anhydride.

Adipic acid, 131.5 g (0.9 moles) was added to diethylenetriamine, 154.8 g (1.5 moles) in a stirred reaction vessel. The mixture was brought to 170°C and held for 3 hours while the water of condensation was removed by distillation. The molten aminoamide was then cooled to 120°C. Using the assumption that all of the carboxyl groups reacted with primary amine, it is calculated that the product contained 1.5 equivalents of secondary amine and 1.2 equivalents of primary amine in 254 g.

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To the entire amount of the aminoamide at 120°C was added 195.6 g (0.6 moles) of predominately hexadecenylsuccinic anhydride (ASA 100, obtained from Dixie Chemical Company, Houston, Texas), containing 95-98% C<sub>16</sub> succinic anhydride, the remainder being a mixture of higher alkenyl succinic anhydrides. The temperature was maintained at 124°C for 2 hours. The product after cooling had an acid number of 25 mg KOH/g and an amine number of 4.05 meq/g (equating to an amine equivalent weight of 247).

### Example 2

This example describes the preparation of a crosslinked hydrophobically modified cationic resin composition by reaction of epichlorohydrin with the hydrophobically modified aminoamide prepared in Example 1.

The aminoamide of Example 1 (98.5 g, 0.40 equivalents of amine) was crushed and dispersed in 281 g of water. Epichlorohydrin (43.2 g, 0.47 moles) was then slowly added to the dispersion while the temperature was maintained at below about 40°C. The resulting reaction mixture was then stirred for 30 minutes at 40°C and then crosslinked by heating at 85°C for 2 hours. The crosslinked resin was homogenized hot using a laboratory homogenizer, and then cooled to room temperature. The product contained 19.1% total solids, had pH 5.02 and particle size of 0.50 microns. It contained 0.70% 1,3-dichloropropan-2-ol, 0.19% 2,3-chloropropanediol, and less than 0.01% residual epichlorohydrin.

### Example 3

This example describes the preparation of a crosslinked, hydrophobically modified cationic resin composition by reaction of epichlorohydrin with the hydrophobically modified aminoamide prepared in Example 1 in an organic solvent.

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The hydrophobically modified aminoamide of Example 1 (97.6 g, 0.39 equivalents of amine) was crushed and dissolved in a mixture of toluene (440 g) and ethanol (496 g). Deionized water (468 g) was added to the solution of aminoamide to form a dispersion.. Epichlorohydrin (43.4 g, 0.47 moles) was then slowly added to the dispersion while the temperature was maintained at below about 40°C. The resulting reaction mixture was then stirred for 2 hours at 40°C and then crosslinked by heating to reflux at 75°C for 2 hours. The crosslinked resin was cooled to 20°C, further diluted with water (1180 g), blended and homogenized using a laboratory homogenizer. The solvent was removed by distillation. The product contained 10.8% total solids, had pH 6.6 and particle size 0.047 microns. It contained 0.48% 1,3-dichloropropan-2-ol, 0.12% 2,3-chloropropanediol, and less than 0.01% residual epichlorohydrin.

#### Example 4

This example illustrates preparation of an aminoamide from adipic acid and diethylenetriamine modified by reaction with the hydrophobizing agent hexadecenylsuccinic anhydride.

Adipic acid (65.77 g, 0.45 moles) was added to diethylenetriamine (77.35 g, 0.75 moles) in a stirred reaction vessel. The mixture was brought to 170°C and held at this temperature for 3 hours while the water of condensation was removed by distillation. The molten product was cooled to 123°C, and then there was added 97.8 g (0.3 moles) of hexadecenylsuccinic anhydride (Accosize®18, from Cytek Industries, West Patterson, New Jersey). The resulting mixture was held at 125°C for 1 hour, at 146°C for 1 hour, and then quenched by addition of water. The product aminoamide had an amine number of 4.51 meq/g (amine equivalent weight, 222) and acid number of 38. The molecular weight determined by SEC was 756 number average and 1468 weight average. The product was diluted with enough water to produce a dispersion with 23.3% solids as measured in a 150°C oven. The dispersion had a pH of 10.2.

### Example 5

A crosslinked hydrophobically modified cationic resin composition was prepared from the hydrophobically modified aminoamide of Example 4. The dispersed hydrophobically modified aminoamide (125.4 g, 29.2 g solids, 0.13 amine equivalents) was blended with 65.1 g of water. Epichlorohydrin (11.1 g, 0.12 moles) was slowly added while keeping the temperature below 40°C. The resulting reaction mixture was stirred for 30 minutes at 40°C and then crosslinked by heating at 65°C for 2 hours, after which it was quenched and diluted by adding enough water to bring the mixture to about 15% solids.

The product was divided into two portions. The first was homogenized using a laboratory homogenizer at room temperature. The second had no further treatment. The product from the first part had 15.1% solids, pH 5.4 and particle size 0.13 microns. The product of the second part had 15.1% solids, pH 5.4, particle size 0.15 microns and contained 0.16% 1,3-dichloropropan-2-ol, 0.07% 2,3-chloropropanediol and less than 0.01% residual epichlorohydrin. Potassium sorbate (0.1%) was added to both portions as a biocide.

### Example 6

This example demonstrates the surface sizing efficiency of products of Examples 2 and 3 of this invention compared to conventional commercial sizing agents.

Waterleaf paper was prepared on a trial paper machine at a basis weight of 64.9 kg /1,000 m<sup>2</sup> from a 50:50 blend of bleached kraft hardwood and softwood pulps. The paper was prepared at a papermaking pH of 8.0 and contained 0.5% alum (based on dry pulp). The paper was unfilled and was not surface treated.

The paper was treated with an aqueous dispersion of resin using a laboratory size press operating at room temperature. The resin level required in the aqueous dispersion to achieve the desired sizing agent level in the paper was determined by first determining the amount of absorbed water picked up



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when the paper was treated with water only in the size press. The level of the resin in the dispersion was then adjusted accordingly to give the desired level of addition to the paper. The paper was drum dried at 104°C immediately following treatment.

5           Sizing was measured after storing the paper for 1 week, using the Hercules Size Tester (Hercules Incorporated., Wilmington, DE) at 80% reflectance with an ink containing 1% formic acid and a green dye. (Reference: The Sizing of Paper, Second Edition, W. F. Reynolds editor, TAPPI Press, 1989). Higher values correspond to higher sizing. The  
10       commercial sizing agents used for comparison were Scripset®740 styrene maleic anhydride copolymer from Monsanto Corp., St. Louis, MO and Hercon®70 alkylketene dimer based sizing agent from Hercules Incorporated, Wilmington, DE). Alkylketene dimers are known to impart slip related  
15       problems to paper when applied to the surface of the sheet in sufficient quantities.

**TABLE 1****HST Sizing (seconds to 80% reflectance)****Sizing Agent Level (Dry Basis)**

<u>Sizing Agent</u>	<u>0.05%</u>	<u>0.1%</u>	<u>0.2%</u>
20       Product of Example 2	6	91	218
Product of Example 3	2.5	83	298
Scripset®740	1	9	62
Hercon®70	308	494	590

25           The data in Table 1 show that the resins of this invention give sizing at levels between the two common commercial sizing agents, Scripset®740 and Hercon®70 .

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### Example 7

This example illustrates preparation of an aminoamide from adipic acid and diethylenetriamine modified by reaction with hexadecenylsuccinic anhydride hydrophobizing agent. Adipic acid (66.0 g, 0.45 moles) was added  
5 to diethylenetriamine (77.4 g, 0.75 moles) in a stirred reaction vessel. The mixture was brought to 170°C and held at this temperature for 3 hours while the water of condensation was removed by distillation. The molten product was cooled to 122°C, and then there was added 97.8 g (0.3 moles) of  
10 hexadecenylsuccinic anhydride (ASA 100). The resulting mixture was held at 123°C for 2 hours and then quenched with water. The product aminoamide had an amine number of 4.44 meq/g (amine equivalent weight, 225) and acid  
number of 44. The product was diluted with enough water to produce a dispersion with a measured solids of 20.6%. The dispersion had a pH of 10.6.

### Example 8

15 A crosslinked hydrophobically modified cationic resin composition was prepared from the hydrophobically modified aminoamide of Example 7. The dispersed hydrophobically modified aminoamide (142.0 g, 29.4 g solids, 0.13  
amine equivalents) was blended with 48.6 g of water. Epichlorohydrin (11.1 g, 0.12 moles) was slowly added while keeping the temperature below 40°C. The  
20 resulting reaction mixture was stirred for 30 minutes at 40°C and then crosslinked by heating at 65°C for 2 hours. The hot product was homogenized using a laboratory homogenizer. The product had 20.2% solids, pH 6.2 and  
particle size 0.074 microns. It contained 0.17% 1,3-dichloropropan-2-ol, 0.06% 2,3-chloropropanediol and less than 0.02% residual epichlorohydrin.

### Example 9

25 This example illustrates the reduced tendency to foam of the crosslinked hydrophobically modified cationic resin composition of Example 8 compared to common commercial surface sizing agents.

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The modified laboratory foam cell consisted of a pump and air introduction device to allow air percolation through a starch solution containing the crosslinked hydrophobically modified cationic resin composition. Time for the foam to reach a designated height in a graduated cylinder was recorded.

- 5 The test solution (700 g) contained 0.25% resin (based on dry starch), 0.6% sodium chloride (based on dry starch) added to a 6% solution of Stayco M (A. E. Staley Manufacturing Company, Decatur, IL) prepared by cooking at 95°C for 30 minutes. The commercial sizing agents used for comparison are Scripset®720 and Scripset 740 styrene maleic anhydride copolymers from
- 10 Monsanto Corp., St. Louis, MO. The results, presented in Table 2 are the time for the foam to reach a volume of 1800 ml. Higher values indicate a lower foaming tendency.

**TABLE 2****Time (seconds) to 1800 ml of Foam**

15	<b><u>Sizing Agent</u></b>	<b><u>Time. sec.</u></b>
	Scripset 720	75
	Scripset 740	60
	Product of Example 8	255

**Example 10**

- 20 This example illustrates preparation of an aminoamide from adipic acid and diethylenetriamine modified by reaction with hexadecenylsuccinic anhydride hydrophobizing agent. Adipic acid (54.80 g, 0.375 moles) was added to diethylenetriamine (77.35 g, 0.75 moles) in a stirred reaction vessel. The mixture was brought to 170°C and held at this temperature for 3 hours
- 25 while the water of condensation was removed by distillation. The molten product was cooled to 125°C, and then there was added 91.28 g (0.28 moles) of hexadecenylsuccinic anhydride (ASA 100). The resulting mixture was held at 125°C for 1 hour, at 140°C for 1 hour, and then quenched by addition of water.

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The product had an amine number of 5.60 meq/g (amine equivalent weight, 178) and acid number of 42 (acid equivalent weight, 1,336). It was diluted with enough water to produce a dispersion with 23.4% solids. The dispersion had a pH of 10.4.

5

### Example 11

A crosslinked hydrophobically modified cationic resin composition was prepared from the hydrophobically modified aminoamide of Example 10. The dispersed hydrophobically modified aminoamide (123.3 g, 28.9 g solids, 0.16 amine equivalents) was blended with 65.4 g of water. Epichlorohydrin (11.1 g, 0.12 moles) was slowly added while keeping the temperature below 40°C. The resulting reaction mixture was stirred for 30 minutes at 40°C and then crosslinked by heating at 65°C for 2 hours, after which it was quenched and diluted by adding enough water to bring the mixture to about 15% solids.

15

The product had 15.7% solids, pH 6.0 and particle size 0.070 microns and contained 0.23% 1,3-dichloropropan-2-ol, 0.16% 2,3-chloropropanediol and less than 0.01% residual epichlorohydrin.

### Example 12

20

This example illustrates another preparation of aminoamide from adipic acid and diethylenetriamine followed by reaction with hexadecenylsuccinic anhydride.

25

Adipic acid (54.80 g, 0.375 moles) was added to diethylenetriamine (77.38 g, 0.75 moles) in a stirred reaction vessel. The mixture was brought to 170°C and held at this temperature for 3 hours while the water of condensation was removed by distillation. The molten product was cooled to 125°C, and then there was added 146.7 g (0.45 moles) of hexadecenylsuccinic anhydride (ASA 100). The resulting mixture was held at 125°C for 1 hour, at 140°C for 1 hour, and then quenched by addition of water. The product had an amine number of 3.69 meq/g (amine equivalent weight, 271) and acid number of 57.5

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(acid equivalent weight, 975). The product was diluted with enough water to produce a dispersion with 23.3% solids. The dispersion had a pH of 10.1.

### **Example 13**

A crosslinked hydrophobically modified cationic resin composition was prepared from the hydrophobically modified aminoamide of Example 12. The dispersed hydrophobically modified aminoamide (152.0 g, 35.4 g solids, 0.13 amine equivalents) was blended with 69.3 g of water. Epichlorohydrin (11.1 g, 0.12 moles) was slowly added while keeping the temperature below 40°C. The resulting reaction mixture was stirred for 30 minutes at 40°C and then crosslinked by heating at 65°C for 2 hours, after which it was quenched and diluted by adding enough water to bring the mixture to about 15% solids.

The product had 15.3% solids, pH 5.8 and particle size 2.18 microns and contained 0.084% 1,3-dichloropropan-2-ol, 0.075% 2,3-chloropropanediol and less than 0.01% residual epichlorohydrin.

### **Example 14**

This example illustrates another preparation of aminoamide from adipic acid and diethylenetriamine hydrophobically modified by reaction with hexadecenylsuccinic anhydride.

Adipic acid (58.40 g, 0.40 moles) was added to diethylenetriamine (68.78 g, 0.66 moles) in a stirred reaction vessel. The mixture was brought to 170°C and held at this temperature for 3 hours while the water of condensation was removed by distillation. The molten product was cooled to 128°C, and then there was added 173.7 g (0.53 moles) of hexadecenylsuccinic anhydride (ASA 100). The resulting mixture was held at 125°C for 1 hour, at 140°C for 1 hour, and then quenched by addition of water. The product had an amine number of 2.35 meq/g (amine equivalent weight, 425) and acid number of 54 (acid equivalent weight, 1042). The product was diluted with enough water to produce a dispersion with 24.1% solids. The dispersion had a pH of 9.0.

**Example 15**

A crosslinked hydrophobically modified cationic resin composition was prepared from the hydrophobically modified aminoamide of Example 14. The dispersed hydrophobically modified aminoamide (178.65g, 43.0 g solids, 0.10 amine equivalents) was blended with 80.75 g of water. Epichlorohydrin (7.4 g, 0.08 moles) was slowly added while keeping the temperature below 40°C. The resulting reaction mixture was stirred for 30 minutes at 40°C and then crosslinked by heating at 65°C for 2 hours, after which it was quenched and diluted by adding enough water to bring the mixture to about 15% solids.

The product had 14.8% solids, pH 5.8 and particle size 1.14 microns. It contained 0.12 % 1,3-dichloropropan-2-ol, 0.18 % 2,3-chloropropanediol and less than 0.01 % residual epichlorohydrin.

**Comparative Example A**

This is a comparative example illustrating preparation of an aminoamide from adipic acid and diethylenetriamine hydrophobically modified with hexadecenylsuccinic anhydride using polyamine to dicarboxylic acid ratios described in U.S. Patent No. 3,922,243, but using water as a dispersing medium.

Adipic acid (109.61 g, 0.75 moles) was added to diethylenetriamine (77.38 g, 0.75 moles) in a stirred reaction vessel. The mixture was brought to 160°C and held at this temperature for 5 hours while the water of condensation was removed by distillation. The molten product was cooled to 128°C, and then there was added 97.8 g (0.30 moles) of hexadecenylsuccinic anhydride (ASA 100). The resulting mixture was held at 160°C for 1 hour and then quenched by addition of water to give a nominal 25% solids. The product was in two layers and was not useable for resin preparation.

### **Comparative Example B**

Comparative Example A was repeated, except that in this case milder reaction conditions, i.e., reaction of the hydrophobizing agent at temperatures less than 150°C were applied.

5           Adipic acid (109.61 g, 0.75 moles) was added to diethylenetriamine (77.38 g, 0.75 moles) in a stirred reaction vessel. The mixture was brought to 160°C and held at this temperature until 1/3 of the theoretical water of condensation was removed by distillation. The molten product was cooled to 128°C, and then there was added 97.8 g (0.30 moles) of hexadecenylsuccinic  
10           anhydride (ASA 100). The resulting mixture was held at 125°C for 1 hour and 140°C for 1 hour and then quenched by addition of water to give a nominal 25% solids. The product had an amine number of 3.26 meq/g (amine equivalent weight, 307) and acid number of 33 (acid equivalent weight, 1696). The product had a measured solids of 22.1% and a pH of 8.11.

### **Comparative Example C**

15           A crosslinked hydrophobically modified cationic resin composition was prepared from the hydrophobically modified aminoamide of Comparative Example B. The dispersed aminoamide (155.52g, 34.37 g solids, 0.11 amine equivalents) was blended with 60.73 g of water. Epichlorohydrin (11.10 g,  
20           0.12 moles) was slowly added while keeping the temperature below 40°C. The resulting reaction mixture was stirred for 30 minutes at 40°C and then crosslinked by heating at 65°C for 2 hours, after which it was quenched and diluted by adding enough water to bring the mixture to about 15% solids.

25           The product had 12.5% solids, pH 6.8, particle size 0.32 microns, and contained 0.42% 1,3-dichloropropan-2-ol, 0.45% 2,3-chloropropanediol and less than 0.02% residual epichlorohydrin.

### Comparative Example D

This is a comparative example illustrating preparation of aminoamide from adipic acid and diethylenetriamine hydrophobically modified by reaction with hexadecenylsuccinic anhydride using polyamine to dicarboxylic acid ratios as described in U.S. Patent No. 3,922,243. The milder reaction conditions of this patent were applied.

Adipic acid (73.07 g, 0.50 moles) was added to diethylenetriamine (51.59 g, 0.50 moles) in a stirred reaction vessel. The mixture was brought to 160°C and held at this temperature until 1/3 of the theoretical water of condensation was removed by distillation. The molten product was cooled to 128°C, and then there was added 130.40 g (0.4 moles) of hexadecenylsuccinic anhydride (ASA 100). The resulting mixture was held at 125°C for 1 hour and 140°C for 1 hour and then quenched by addition of water to give a nominal 25% solids. The product had an amine number of 1.53 meq/g (amine equivalent weight, 652) and acid number of 76 (acid equivalent weight, 740). The product had a measured solids of 24.0% and a pH of 5.7.

### Comparative Example E

A crosslinked hydrophobically modified cationic resin composition was prepared from the hydrophobically modified aminoamide of Comparative Example D. The dispersed hydrophobically modified aminoamide (197.71g, 47.41 g solids, 0.07 amine equivalents) was blended with 84.34 g of water. Epichlorohydrin (11.10 g, 0.12 moles) was slowly added while keeping the temperature below 40°C. The resulting reaction mixture was stirred for 30 minutes at 40°C and then crosslinked by heating at 65°C for 2 hours, after which it was quenched and diluted by adding enough water to bring the mixture to about 15% solids.

The product had 14.4% solids, pH 6.0, and particle size 0.28 microns. It contained 0.21 % 1,3-dichloropropan-2-ol, 0.64 % 2,3-chloropropanediol and 0.19 % residual epichlorohydrin.



### Comparative Example F

This is a comparative example illustrating preparation of aminoamide from adipic acid and diethylenetriamine hydrophobically modified by reaction with hexadecenylsuccinic anhydride using polyamine to dicarboxylic acid ratios as described in U.S. Patent No. 3,922,243, but higher than those used in the previous comparative examples. The milder reaction conditions of the patent were applied.

Adipic acid (81.84 g, 0.56 moles) was added to diethylenetriamine (77.38 g, 0.75 moles) in a stirred reaction vessel. The mixture was brought to 170°C and held for 3 hours while the water of condensation was removed by distillation. The molten product was cooled to 129°C, and then there was added 122.25 g (0.375 moles) of hexadecenylsuccinic anhydride (ASA 100). The resulting mixture was held at 125°C for 1 hour and 140°C for 1 hour and then quenched by addition of water to give a nominal 25% solids. The product had an amine number of 2.78 meq/g (amine equivalent weight, 360) and acid number of 49 (acid equivalent weight, 1156). The product had a measured solids of 25.2% and a pH of 9.0.

### Comparative Example G

A crosslinked hydrophobically modified cationic resin composition was prepared from the hydrophobically modified aminoamide of Comparative Example F. The dispersed hydrophobically modified aminoamide (138.46g, 34.88 g solids, 0.10 amine equivalents) was blended with 80.34 g of water. Epichlorohydrin (11.10 g, 0.12 moles) was slowly added while keeping the temperature below 40°C. The resulting reaction mixture was stirred for 30 minutes at 40°C and then crosslinked by heating at 65°C for 2 hours, after which it was quenched and diluted by adding enough water to bring the mixture to about 15% solids.

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The product had 14.2% solids, pH 5.4, and particle size 0.30 microns. It contained 0.04 % 1,3-dichloropropan-2-ol, 0.15 % 2,3-chloropropanediol and less than 0.01 % residual epichlorohydrin.

### Example 16

5           This example demonstrates the sizing efficiency of resins of this invention compared to materials described in U.S. Patent No. 3,922,243.

10           Waterleaf paper was prepared on a trial paper machine. The paper was prepared at a basis weight of 64.9 kg /1,000 m<sup>2</sup> from a 50:50 blend of bleached kraft hardwood and softwood pulps. The paper was prepared at a papermaking pH of 8.0 and contained 0.5% alum and 12% Albacar 5970™ precipitated calcium carbonate (Speciality Minerals Inc., Bethlehem, Pa.). The paper was not surface treated. All additive amounts are on a dry basis based on the dry weight of pulp.

15           The paper was treated with an 8% solution of an GPC D-150 oxidized starch (from Grain Processing Company, Muscatine, IA), also containing the resin of this invention in dispersed form, using a laboratory size press operating at 65° C. The level of resin needed in the starch solution was determined by first determining the amount of adsorbed starch solution when the paper was treated with starch solution only in the size press. The level of resin in the starch solution was then adjusted accordingly to give the desired level of addition to the paper (0.25 %). The sizing solutions were prepared both with (at a level of 0.2% based on paper) and without optical brightener (Phorwite P, Mobay Corp., Pittsburgh, PA). Optical brightening agents are commonly used in the size press to increase the brightness of paper. The paper was drum dried at 25 96°C immediately following treatment.

Sizing results are shown in Table 3. Sizing was measured on the paper after storage for 2 weeks, using the Hercules Size Tester (Hercules, Inc., Wilmington, DE) at 80% reflectance with an ink containing 1% formic acid

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and a green dye. A duplicate of Example 2 was used as the control. The molar ratios of polyamine to dicarboxylic acid and hydrophobizing agent to polyamine used to prepare the hydrophobically modified aminoamide are shown for comparison.

5

**Table 3****Surface Sizing Comparison--HST Sizing (seconds to 80% reflectance)**

<u>Sizing Agent</u>	<u>Amine/Diacid Mole Ratio</u>	<u>Moles Hydrophobe/ Equivalents of Secondary Amine</u>	<u>HST without Optical Brightener</u>	<u>HST with Optical Brightener</u>
Product of Example 2	1.66	0.4	64	56
10 Product of Example 15	1.66	0.8	36	60
Product of Comp. Example E	1.0	0.8	2	24

15 The results in Table 3 demonstrate substantially improved surface sizing when the polyamine to dicarboxylic acid ratios in the aminoamide is greater than about 1.4.

**Example 17**

This example demonstrates the sizing efficiency of the products of this invention compared to materials described in U.S. Patent No. 3,922,243.

20 A waterleaf paper was prepared on a trial papermachine. The paper was prepared at a basis weight of 64.9 kg /1,000 m<sup>2</sup> from a 50:50 blend of bleached kraft hardwood and softwood pulps. The paper was prepared at a papermaking pH of 8.0 and contained 0.5% alum. The paper was not filled and not surface treated. All additive amounts are on a dry basis based on the dry weight of

25 pulp.

The paper was treated with an aqueous dispersion of the resin using a laboratory size press operating at room temperature. The paper was drum

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5 dried immediately following treatment at 104° C. The level of sizing agent needed in the aqueous dispersion was determined by first determining the amount of absorbed water picked up when the paper was treated with water only in the size press. The level of resin in the dispersion was then adjusted accordingly to give the desired level of addition to the paper (0.2%).

Sizing results are shown below in Table 4. Sizing was measured after storing the paper for 1 week, using the Hercules Size Tester at 80% reflectance with an ink containing 1% formic acid and a green dye. A duplicate of Example 2 was used as the control. The molar ratios of polyamine to  
10 dicarboxylic acid and hydrophobizing agent to polyamine used to prepare the hydrophobically modified aminoamide are shown for comparison.

**TABLE 4****Surface Size Comparison--HST Sizing (seconds to 80% reflectance)**

		<u>Amine/Diacid Mole Ratio</u>	<u>Moles Hydrophobe/ Equivalents of Secondary Amine</u>	<u>HST. seconds</u>
15	Product of Example 2	1.66	0.4	>1200
	Product of Example 11	2.00	0.4	1107
	Product of Example 13	2.00	0.8	652
20	Product of Comp. Example C	1.00	0.4	12
	Product of Comp. Example G	1.33	0.5	513

25 The data in Table 4 indicate the higher levels of sizing that are obtained with the resins of this invention when compared to resins prepared by the methods of U.S. Patent No. 3,922,243.

### Comparative Example H

This example describes preparation of a bis-stearamide.

Stearic acid (Emersol®152, from Henkel Corporation, Cincinnati, Ohio),

5 512.1 g (1.8 moles), was melted in a stirred reaction vessel and heated to 106°C. To this was slowly added diethylenetriamine (103.2 g, 1.0 moles). The mixture was brought to 170°C and held at this temperature for 3 hours while water of condensation was removed by distillation. The molten product was cooled. The product had a melting point of 105°C and an amine number of  
10 2.02 meq/g (amine equivalent weight, 495).

### Comparative Example J

This example describes preparation of a crosslinked cationic resin composition from the bis-stearamide of Comparative Example H.

The molten bis-stearamide (97.0 g, 0.20 amine equivalents) of  
15 Comparative Example H was slowly blended into hot water (1200 ml) to form a dispersion. The temperature of the dispersion was set at 85° C and epichlorohydrin (18.5 g, 0.20 moles) was rapidly added. The mixture was stirred for 2 hours, after which it was homogenized and then cooled to room temperature.

20 The product had 8.2% solids, pH 4.0, and particle size 0.40 microns.

### Example 18

This example demonstrates the sizing efficiency and impact on sheet properties of products of this invention compared to a sizing agent based on bis-stearamide and to conventional commercial sizing agents.

25 Paper was prepared on a trial papermachine with sizing agents added both internally and to the surface of the sheet at the size press. The paper was prepared at a basis weight of 64.9 kg /1,000 m<sup>2</sup> from a 75:25 blend of bleached kraft hardwood and softwood pulps refined to 425 CSF. The paper was

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prepared at a papermaking pH of 8.0, contained 0.25% alum (based on pulp), was filled with Albacar 5970 precipitated calcium carbonate at 10%, and was surface treated with a size press solution containing 4% Stayco M oxidized starch and 0.05% sodium chloride at 55°C. For surface application, the solids level of resin and sodium chloride needed to apply the desired amount of material was determined by first determining the amount of absorbed starch solution picked up when the paper was treated with starch solution only in the size press. The level of resin and sodium chloride in the starch solution was then adjusted accordingly to give the desired level of addition to the paper. The paper was dried to give 4-6% moisture at the reel.

Sizing agent was applied either internally or in the size press solution. The base sheet had at least 0.05% of Hercon®70 alkylketene dimer sizing agent in all sheets to aid in size press operation. Sizing and coefficient-of-friction (COF) results are shown in Table 5. All results were measured after storing the paper for 1 week. Sizing was measured using the Hercules Size Tester (Hercules, Inc., Wilmington, DE) at 80% reflectance with an ink containing 1% formic acid and a green dye. COF was measured using a Thwing-Albert (Thwing-Albert Instrument Company, Philadelphia, PA) in the machine direction, felt-to-wire, using a 200 g sled. The static COF is shown. A sizing agent equivalent to that in Example 3 was used as the control. Alkylketene dimers and bis-stearamides are known to cause slip related problems in paper when applied to the surface of the sheet, or internally, in sufficient quantities.

**TABLE 5****Impact on Sizing Efficiency and Sheet Properties<sup>1</sup>**

	<u>Sizing Agent</u>	<u>Size Addition Level (%)</u>	<u>Size Addition Point</u>	<u>HST, sec.</u>	<u>COF, Static</u>
	Hercon 70	0.05	internal	2	0.482
5	"	0.075	internal	166	0.510
		0.10	internal	272	0.500
	Example 3	0.025	surface	41	0.575
	"	0.10	surface	152	0.502
	"	0.10	internal	43	0.525
	"	0.20	internal	83	0.532
10	Comp. Example J	0.025	surface	9	0.542
	"	0.10	surface	229	0.315
	"	0.10	internal	172	0.478
	"	0.20	internal	236	0.395

15

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1. Hercon 70 is in all sheets at 0.05% unless otherwise indicated.

20

The data in Table 5 show that resins as described herein impart a significant level of sizing to paper when used in combination with a low level of internal size, without negatively impacting the coefficient-of-friction of paper. The bis-stearamide size, Comparative Example J, imparts sizing but also has a large negative impact on the coefficient-of-friction of paper. Commercial experience shows that high levels of alkylketene dimer based sizing agents also can negatively impact the coefficient-of-friction of paper and the performance of paper in high speed converting, as discussed by C.L. Brungardt and J.C. Gast, Proceedings of the TAPPI 1996 Papermakers Conference, p. 297.

25

### Example 19

This example illustrates the preparation of an aminoamide from adipic acid and diethylenetriamine hydrophobically modified by reaction with stearic acid.

5           Adipic acid, 65.7 g (0.45 moles) was added to diethylenetriamine, 77.4 g (0.75 moles) in a stirred reaction vessel. The mixture was brought to 170°C and held for 3 hours while the water of condensation was removed by distillation. The molten aminoamide was then cooled to 125°C.

10           To the entire amount of the aminoamide at 125°C was added 85.3 g (0.3 moles) of 95% stearic acid (Aldrich Chemical Co., Milwaukee, WI). The temperature was raised to 170°C for 2 hours. The product was diluted with hot water to give a nominal total solids of 23.0%. The product had a measured total solids of 21.9%, pH 10.4, an acid number of 13 mg KOH/gm and an amine number of 5.39 meq/g (equating to an amine equivalent weight of 185).  
15           The number average molecular weight by SEC was 790.

### Example 20

          This example describes the preparation of a crosslinked hydrophobically modified cationic resin composition by reaction of epichlorohydrin with the hydrophobically modified aminoamide prepared in  
20           Example 19.

          The dispersed hydrophobically modified aminoamide of Example 19 (674.4 g, 147.7 g solids, 0.8 equivalents of amine) was blended with 308.7 g of water. Epichlorohydrin (61.1 g, 0.66 moles) was then slowly added to the dispersion while the temperature was maintained at below about 40°C. The  
25           resulting reaction mixture was then stirred for 30 minutes at 40°C and then crosslinked by heating at 65°C for 2 hours, after which it was quenched and diluted by adding enough water to bring the mixture to about 10.5% solids.



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The product contained 10.7% total solids, had pH 5.91, and particle size of  $\approx 1.00$  microns. It contained 0.076% 1,3-dichloropropan-2-ol, 0.04% 2,3-chloropropanediol, and less than 0.01% residual epichlorohydrin.

5        Surface sizing with the product resin was evaluated using the same procedures as described in Example 18 except that the paper was prepared at 75.0 kg/1000 m<sup>2</sup> and internal addition of Hercon 70 was at 0.075% based on dry pulp. Under these conditions the sizing agent (0.2%, based on paper) of this example gave 217 seconds HST sizing when added to the size press starch compared to 1 second HST sizing with the internal size and size press starch  
10       alone.

      It is not intended that the examples presented here should be construed to limit the invention, but rather they are submitted to illustrate some of the specific embodiments of the invention. Various modifications and variations of the present invention can be made without departing from the scope of the  
15       appended claims.

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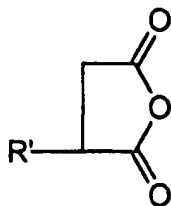
What is claimed is:

1. A resin composition comprising the reaction product of epihalohydrin and hydrophobically modified aminoamide obtained by the reaction of:

5 (a) aminoamide containing at least one primary amine group and at least one non-primary amine group selected from the group consisting of secondary and tertiary amine groups, the aminoamide being obtained by reaction of an amine composition comprising polyamine containing at least two primary  
10 amine groups and at least one amine group selected from the group consisting of secondary and tertiary amine groups, with dicarboxylic acid or derivatives thereof, wherein the molar ratio of polyamine to dicarboxylic acid or derivative thereof, is from about 1.5:1 to about 3:1, and

(b) hydrophobizing agent having from about 12 to about 40 carbon atoms, wherein the amount of hydrophobizing agent employed is sufficient to  
15 react with at least a portion of the primary amine groups, but insufficient to react with more than about 60% of the non-primary amine groups of the aminoamide.

2. The resin composition of claim 1 wherein the hydrophobizing agent comprises at least one member of the group consisting of: i)  
20 monocarboxylic acids, or derivatives thereof; ii) dicarboxylic acid anhydrides having the formula



(I)

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wherein R' is a straight chain or branched, saturated or unsaturated alkyl radical having from about 8 to about 22 carbon atoms; iii) ketene dimers or multimers; and iv) mixtures thereof.

5           3.     The resin composition of claim 1 wherein the molar ratio of polyamine to dicarboxylic acid, or derivatives thereof, is from 1.55:1 to 2.5:1.

          4.     The resin composition of claim 1 wherein the molar ratio of polyamine to dicarboxylic acid, or derivatives thereof, is from 1.6:1 to 2:1.

10           5.     The resin composition of claim 1 wherein at least 50 mole percent of the amine composition comprises polyamine containing at least two primary amine groups and at least one amine group selected from the group consisting of secondary and tertiary amine groups.

15           6.     The resin composition of claim 1 wherein the polyamine comprises at least one member selected from the group consisting of N-alkyl bis(3-aminopropylamine) wherein the N-alkyl group contains from 1 to about 12 carbon atoms, and polyalkylene polyamines containing two primary amine groups and at least one secondary amine group, the nitrogen atoms being linked together by groups of the formula  $-C_nH_{2n}-$  where n is from 2 to 6.

20           7.     The resin composition of claim 6 wherein the polyamine is polyalkylene polyamine containing two primary amine groups and at least one secondary amine group where the nitrogen atoms are linked together by groups of the formula  $-C_nH_{2n}-$  where n is from 2 to 6.

          8.     The resin composition of claim 7 wherein the polyalkylene polyamine is at least one member selected from the group consisting of

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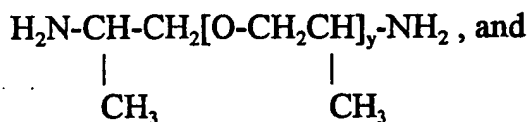
polyethylenepolyamines, polypropylenepolyamines and polybutylenepolyamines.

9. The resin composition of claim 7 wherein the polyalkylene polyamine is at least one member selected from the group consisting of  
5 diethylenetriamine, triethylenetetramine and tetraethylenepentamine.

10. The resin composition of claim 6 wherein the N-alkyl bis(3-aminopropylamine) is methyl bis(3-aminopropylamine).

11. The resin composition of claim 5 wherein the amine composition further comprises diamine selected from the group consisting of

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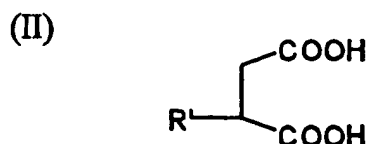
wherein x is an integer from 2 to about 10, y is an integer from 2 to about 100, b is an integer from 2 to about 100, and a and c, which can be the same or different, are integers from 0 to about 5.

12. The resin composition of claim 1 wherein the dicarboxylic acid derivatives are selected from the group consisting of esters, anhydrides and acid halides.

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13. The resin composition of claim 1 wherein the dicarboxylic acid comprises an aliphatic, alicyclic or aromatic dicarboxylic acid containing from 2 to about 44 carbon atoms, or a derivative thereof.

5 14. The resin composition of claim 13 wherein the dicarboxylic acid is at least one member selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, fumaric acid, maleic acid, phthalic acid, terephthalic acid, diglycolic acid, C<sub>36</sub> dimer acid, and dicarboxylic acid having the formula



10 or derivatives thereof, wherein R' is a straight chain or branched, saturated or unsaturated alkyl radical having from about 8 to about 22 carbon atoms.

15 15. The resin composition of claim 14 wherein the dicarboxylic acid is at least one member selected from the group consisting of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid and azelaic acid.

16. The resin composition of claim 14 wherein the derivative of dicarboxylic acid of formula (II) is the cyclic anhydride.

17. The resin composition of claim 13 wherein the dicarboxylic acid is adipic acid, or a derivative thereof.

20 18. The resin composition of claim 17 wherein the dicarboxylic acid is adipic acid.

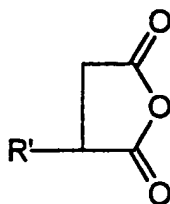
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19. The resin composition of claim 1 wherein the polyamine comprises diethylenetriamine and the dicarboxylic acid comprises adipic acid, or a derivative thereof.

5 20. The resin composition of claim 2 wherein the hydrophobizing agent is monocarboxylic acid, or a derivative thereof, of the formula  $\text{RCOOH}$  where the R group is selected from the group consisting of alkyl, alkenyl, aryl, cycloalkyl and cycloalkenyl.

10 21. The resin composition of claim 20 wherein the monocarboxylic acid derivatives are selected from the group consisting of esters, anhydrides, acid halides and isocyanates.

22. The resin composition of claim 2 wherein the hydrophobizing agent is a substituted succinic anhydride of the formula:



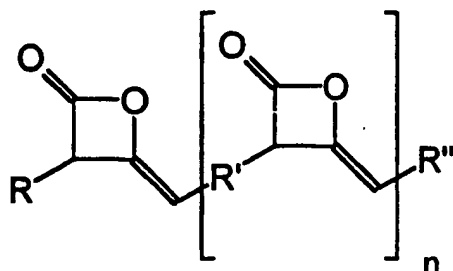
(I)

15 where R' is selected from the group consisting of branched or straight chain alkyl, branched or straight chain alkenyl, cycloalkyl, aralkyl and aralkenyl hydrocarbons containing from about 8 to about 22 carbon atoms.

23. The resin composition of claim 2 wherein the hydrophobizing agent is the reaction product of maleic anhydride with  $\text{C}_{16}$ - $\text{C}_{18}$  olefins.

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24. The resin composition of claim 2 wherein the hydrophobizing agent is ketene dimer or multimer of structure:



(VI)

5 wherein n is an integer of 0 to about 20, R and R'', which may be the same or different, are saturated or unsaturated straight chain or branched alkyl groups having 8 to 24 carbon atoms; and R' is a saturated or unsaturated straight chain or branched alkyl group having from about 5 to about 40 carbon atoms.

10 25. The resin composition of claim 1 wherein the amount of hydrophobizing agent employed is insufficient to react with more than about 30% of the non-primary amine groups of the aminoamide, when the polyaminoamide contains secondary amine groups.

15 26. The resin composition of claim 25 wherein the amount of hydrophobizing agent employed is insufficient to react with more than about 10% of the non-primary amine groups of the aminoamide.

27. The resin composition of claim 1 wherein the amount of hydrophobizing agent employed is sufficient to react with at least 20% of the primary amine groups.

20 28. The resin composition of claim 1 wherein the epihalohydrin comprises epichlorohydrin.

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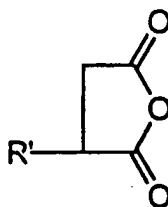
29. The resin composition of claim 1 which has been crosslinked.

30. The resin composition of claim 1 wherein at least 40% of the amine groups of the hydrophobically modified aminoamide have been reacted with epihalohydrin.

5 31. The resin composition of claim 30 wherein at least 70% of the amine groups of the hydrophobically modified aminoamide have been reacted with epihalohydrin.

10 32. The resin composition of claim 31 wherein at least 90% of the amine groups of the hydrophobically modified aminoamide have been reacted with epihalohydrin.

33. The resin composition of claim 1 wherein the polyamine comprises diethylenetriamine; the dicarboxylic acid comprises adipic acid, or a derivative thereof; the epihalohydrin is epichlorohydrin; the hydrophobizing agent comprises a substituted succinic anhydride having the formula



15 where R' is a branched or straight chain alkenyl group containing from 8 to about 22 carbon atoms, the amount of hydrophobizing agent being sufficient to react with at least 20% of the primary amine groups; and wherein at least 70% of the secondary amine groups have been reacted with epichlorohydrin.



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34. A method for preparing a resin composition comprising:

a) reacting an amine composition comprising polyamine containing at least two primary amine groups and at least one amine group selected from the group consisting of secondary and tertiary amine groups with dicarboxylic acid, or derivatives thereof, wherein the molar ratio of polyamine to dicarboxylic acid or derivative thereof is greater than 1.4:1, to form aminoamide containing at least one primary amine group and at least one non-primary amine group selected from the group consisting of secondary and tertiary amine groups;

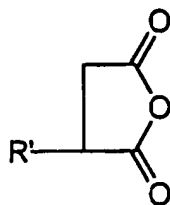
b) reacting the aminoamide with hydrophobizing agent having from about 12 to about 40 carbon atoms to form hydrophobically modified aminoamide,

wherein the amount of hydrophobizing agent employed is sufficient to react with at least a portion of the primary amine groups, but insufficient to react with more than about 60% of the non-primary amine groups of the aminoamide; and

c) reacting the hydrophobically modified aminoamide with epihalohydrin.

35. The method of claim 34 wherein the epihalohydrin comprises epichlorohydrin.

36. The method of claim 34 wherein the hydrophobizing agent comprises at least one member selected from the group consisting of: i) monocarboxylic acids, or derivatives thereof; ii) dicarboxylic acid anhydrides having the formula:



(I)

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30 wherein R' is a straight chain or branched, saturated or unsaturated alkyl radical having from about 8 to about 22 carbon atoms; iii) ketene dimers; iv) ketene multimers; and v) mixtures thereof.

37. The method of claim 34 wherein steps (a) and (b) are carried out neat.

35 38. The method of claim 34 wherein steps (a) and (b) are carried out in solvent.

39. The method of claim 34 wherein step (c) is carried out in aqueous medium.

40 40. The method of claim 36 wherein the hydrophobizing agent has the structure of formula I and the temperature during reaction of the aminoamide with hydrophobizing agent is from about 100°C to about 150°C.

41. The method of claim 34 further comprising (d) crosslinking the resin composition by heating it at a temperature of from about 40°C to about 90°C.

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42. A resin composition prepared by the method of claim 34.

43. A method for sizing paper comprising adding to the surface of a paper sheet an aqueous suspension of the resin composition of claim 1.

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44. A method for sizing paper comprising adding to the surface of a paper sheet an aqueous suspension of the resin composition of claim 29.

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45. Sized paper made by the process of claim 43.

46. Sized paper made by the process of claim 44.

5           47. A method for preparing sized paper comprising the steps of (a) providing an aqueous pulp suspension; (b) adding to the aqueous pulp suspension an aqueous suspension of the resin composition of claim 1; (c) forming the pulp into a sheet; and (d) drying the sheet to obtain sized paper.

10           48. A method for preparing sized paper comprising the steps of (a) providing an aqueous pulp suspension; (b) adding to the aqueous pulp suspension an aqueous suspension of the crosslinked resin composition of claim 29; (c) forming the pulp into a sheet; and (d) drying the sheet to obtain sized paper.

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49. Paper prepared by the method of claim 47.

50. Paper prepared by the method of claim 48.

## INTERNATIONAL SEARCH REPORT

national Application No

PCT/US 98/03358

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G73/02 D21H21/16 D21H17/56

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 922 243 A (ALDRICH PAUL H ET AL) 25 November 1975 cited in the application see claims 1-4	1-50
A	US 5 314 721 A (MUELLER MICHAEL ET AL) 24 May 1994 see claims 1-3	1-50
A	US 4 478 682 A (BANKERT RALPH A ET AL) 23 October 1984 see claims 1-3	1-50



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

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"&amp;" document member of the same patent family

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2 June 1998

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/03358

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